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(54) Adhesives comprising  
polypropylene, polyethylene and  
acid-grafted polyethylene

(57) A modified polyolefin adhesive  
blend comprises:

(a) 0.1 to 40 parts of a graft  
copolymer of 70 to 99.999% of a  
polyethylene backbone grafted with  
30 to 0.001% of at least one

polymerizable ethylenically  
unsaturated carboxylic acid or  
anhydride, and

(b) 99.9 to 60 parts of a mixture of  
25 to 75% of linear low density  
polyethylene and 75 to 25% of  
polypropylene. It can be used to bond  
similar or dissimilar materials, such as  
polypropylene, nylon, ethylene-vinyl  
alcohol copolymer and metals, to form  
composite structures.

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## SPECIFICATION

## Adhesive blends and composite structures comprising same

This invention is concerned with modified polyolefin adhesive blends and with composite structures comprising the same.

5 Composite structures of polypropylene (PP) and polar substrates are increasingly used in industry at the present time. One solution to the problem of securely adhering polypropylene to polar substrates, such as nylon, ethylene-vinyl alcohol copolymers (EVOH), polyvinyl alcohol polymers, metals, glass or wood, is to blend a polypropylene grafted with an unsaturated carboxylic acid or acid derivative with polypropylene and use this mixture directly as an adhesive layer between the polypropylene and the 10 polar substrate. It would sometimes be preferable to use polyethylene grafted with an unsaturated carboxylic acid or acid derivative because such grafted polyethylenes are easier to prepare than grafted polypropylenes.

If polyethylene graft copolymers are blended with polypropylene, however, relatively poor adhesion is obtained to polar polymers and other polar substrates; in some instances no adhesion at all 15 is obtained.

We have now found that by grafting suitable unsaturated carboxylic acids or acid anhydrides to a polyethylene backbone and blending the resulting graft copolymer with a mixture of a polyethylene homo- or co-polymer made by low pressure polymerization (usually designated as linear low density polyethylene or LLDPE) and a polypropylene, the resulting blend has excellent adhesive strength to both 20 polypropylene and to various polar substrates, including polar polymers such as nylon, ethylenevinyl alcohol copolymers, and polyvinyl alcohol polymers, and other polar surfaces, such as metals, glass, cellophane, paper, and wood.

According to the present invention, therefore, there is provided a modified polyolefin adhesive blend, which comprises, by weight:

25 (a) 0.1 to 40 parts of a graft copolymer of 70 to 99.999% of a polyethylene backbone grafted with 30 to 0.001% of at least one polymerizable ethylenically unsaturated carboxylic acid or carboxylic acid anhydride, and

(b) 99.9 to 60 parts of a blending resin mixture of 25 to 75% of a linear low density polyethylene and 75 to 25% of a polypropylene.

30 The polyethylene used for the grafting backbone may be a homopolymer of ethylene or a copolymer of ethylene with propylene, butene-1 and other unsaturated aliphatic hydrocarbons. Blends of two or more of such homopolymers and/or copolymers may also be used.

The polypropylene used as part of the blending resin may be a propylene homopolymer or a copolymer of propylene with ethylene, butene and other unsaturated aliphatic hydrocarbons. Such 35 homopolymers and copolymers are usually prepared using transition metal catalysts. It is particularly preferred to use propylene copolymers prepared by the so-called block copolymerization process. Blends of two or more of such homopolymers and/or copolymers may also be used as the polypropylene component of the blending resin.

As is known, linear low density polyethylenes are copolymers of ethylene with up to 40% of a 40 higher olefin, such as propylene, butene-1, hexene-1, or octene-1. Blends of two or more of such linear low density polyethylenes may also be used. Such ethylene copolymers are prepared by the low pressure method; they are also known as low pressure low density polyethylenes (LLDPE). It is particularly preferred to use those linear low density polyethylenes that have a narrow molecular weight distribution.

45 These linear low density polyethylenes have a unique set of properties which distinguish them from both conventional low density polyethylenes (LDPE) and high density polyethylenes. Because of the methods by which conventional low density polyethylenes are prepared, they are highly branched materials which have a tendency to coil on themselves and when stretched out snap back and exclude other materials. The linear low density materials, on the other hand, as their name indicates, have very 50 little of this long-chain branching and have on the backbone just short-chain branches introduced by the use of a comonomer. For this reason these polymers have melting points approximately 15—20° higher than those of conventional LDPE resins.

The linear structure allows the polymer to stretch out better and also to blend more easily with other polymers having a linear structure, such as polypropylenes, polyethylenes and polybutene-1. The 55 range of density for linear low density polyethylenes is from 0.91 to less than 0.94. This distinguishes LLDPE from HDPE, the density of which ranges from 0.94 to 0.97. The structure of linear low density polyethylenes differs from that of high density materials by the fact that the former contain considerably more of the comonomer (leading to a high degree of short chain branching) than the latter. This difference in structure causes their properties to differ from those of HDPE and LDPE.

60 Linearity leads to good tensile and tear properties, while branching yields toughness, puncture resistance and tear strength, low temperature impact, low warpage and excellent environmental stress crack resistance. These differences from conventional low density polyethylene and high density polyethylene have caused LLDPE to be called a third generation of polyethylene — a different material, actually a hybrid with its own set of properties. Because it has its own set of properties, one cannot per

se extrapolate and predict the properties of this material, when combined with other polymers, on the basis of the behaviour of HDPE or LDPE in blends. It was therefore surprising to find that these materials, when combined with polyethylene-graft copolymers and polypropylene give blends having properties which cannot be obtained by using LDPE or HDPE combined in the same way with polypropylene and a polyethylene-graft copolymer.

The backbone of the graft copolymers used according to the invention may be a homopolymer of ethylene and a copolymer of ethylene with, preferably, up to 40 weight % of such higher olefins as propylene, 1-butene and 1-hexene and may contain up to 5% of a dior triolefin such as are used commercially in ethylene-propylene terpolymers, such as ethylenenorbornene, methylenenorbornene, 1,4-hexadiene and vinylnorbornene. The backbone polymer may also be a blend of two or more of such homopolymers, copolymers or terpolymers.

Suitable unsaturated carboxylic acids or acid anhydrides for use as the grafting monomer include for example, acrylic acid, methacrylic acid, maleic anhydride, 4-methyl cyclohex-4-ene-1,2-dicarboxylic acid anhydride, bicyclo(2.2.2)oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,3-dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro(4,4)non-7-ene, bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, maleopimaric acid, tetrahydrophthalic anhydride, x-methylbicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, x-methylnorborn-5-ene-2,3-dicarboxylic acid anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride. Nadic anhydride methyl Nadic anhydride, Himic anhydride, methyl Himic anhydride and other fused ring monomers described in U.S. Patents 3,873,643 and 3,882,194.

Cografting monomers as described in U.S. Patent 3,882,194 can also be used for preparing the graft copolymers of this invention.

Suitable conjugated unsaturated esters suitable for cografting include, for example, dialkyl maleates, dialkyl fumarates, dialkyl itaconates, dialkyl mesaconates, dialkyl citraconates, alkyl acrylates, alkyl crotonates, alkyl tiglates and alkyl methacrylates, where alkyl is an aliphatic, aryl-aliphatic or cycloaliphatic group containing 1—12 carbon atoms. Particularly suitable esters for such cografted copolymers are dibutyl maleate, diethyl fumarate and dimethyl itaconate. Among the acids and acid anhydrides particularly useful in such cografted copolymers are maleic anhydride, tetrahydrophthalic anhydride, x-methylbicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride and bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride.

More than one monomer in either or both classes of monomer may be used in order to control the physical properties of the final products. Grafting is, in general, effected by heating a mixture of the polymer or polymers and the monomer or monomers with or without a solvent. The mixture can be heated to above the melting point of the polyolefin with or without a catalyst. Thus grafting may be effected in the presence of air, hydroperoxides, other free radical catalysts or in the essential absence of these materials where the mixture is maintained at elevated temperatures and (if no solvent is used) preferably under high shear.

The graft and cograft copolymers used according to the invention are recovered by any method or system which separates or utilizes the graft copolymer obtained. Thus, the copolymer may be recovered in the form of precipitated fluff, pellets, powders and the like, as well as further chemically reacted or blended pellets, powders and the like or in the form of shaped articles formed directly from the resulting copolymer.

Any of the commonly known hydroperoxides which have a half life of at least 1 minute at 145°C may be used in making the graft copolymer. Such hydroperoxides have the general formula  $R-O-OH$ , wherein R is an organic radical. Suitable hydroperoxides include, for example, t-butyl hydroperoxide, p-menthane, hydroperoxide, pinane hydroperoxide, and cumene hydroperoxide. The elevated temperature used in grafting causes rapid decomposition of the hydroperoxide which catalyzes the reaction between the polyolefin and monomer to form the graft copolymer.

Obviously, the more homogeneous the mixture prior to heating, the less mixing of the solution or molten composition will be required. It has been found, in general, that in order to obtain a desirable degree of conversion, some form of mixing is highly desirable in the absence of a solvent, even when a uniform mixture of all the components of the reaction mixture is formed prior to heating. In general, when a solvent is not used, the composition should be heated to a temperature above about 130°C, and it is preferred to use a temperature of from 200° to 360°C. Temperatures substantially above about 360°C are generally to be avoided in order to avoid substantial decomposition of the polymeric ingredients. However, if the decomposition products are not undesirable in the product, as in the production of high melt index waxes, higher temperatures may be employed. The reaction time required is quite short, being from a few seconds to about twenty minutes, although extended heating times do not substantially affect the product and may be employed when desired for any reason.

A convenient method of accomplishing the reaction is to premix the ingredients of the reaction mixture and then extrude the composition through a heated extruder. Other mixing means, such as a Brabender mixer, a Banbury mixer, roll mills and the like may also be employed for the process. In order to prevent undue increase in molecular weight with a possibility of some crosslinking at elevated temperatures, it is desirable to carry out the reaction in a closed vessel. A conventional single or multiple screw extruder accomplishes this result without the use of auxiliary equipment and for this

reason is a particularly desirable reaction vessel.

The resulting copolymers should consist of 70 to 99.95 weight % of polyethylene and, complementally, 0.05 to 30 weight % of the unsaturated acid or acid anhydride or mixtures.

The cogaft copolymers used in the invention consist of 50 to 99.9 weight % of polyolefin, 0.05 to 25 weight % of the unsaturated acid or acid anhydride or mixtures thereof, and 0.05 to 25 weight % of the unsaturated ester and mixtures thereof. These graft copolymers are capable of being blended or reacted with a wide variety of other materials to modify the copolymer further.

The blends of this invention can be used to join polypropylene to a number of polar materials or to join two polar materials together. Bonding can be effected by lamination, coextrusion, extrusion lamination, coextrusion coating or any other method for joining dissimilar materials known to those skilled in the art. Composite materials which can be made in this way include, for example, polypropylene/adhesive of this invention/nylon, polypropylene/adhesive/ethylene-vinyl alcohol copolymer, polypropylene/adhesive/aluminium, polypropylene/adhesive/steel, polypropylene/adhesive/glass, polypropylene/adhesive/wood, polypropylene/adhesive/leather, polypropylene/adhesive/nylon/adhesive/polypropylene, and polypropylene/adhesive/EVOH/adhesive/polypropylene.

Examples of other metal combinations are aluminium/adhesive/aluminium or adhesive/aluminium/adhesive or polypropylene/adhesive/aluminium/adhesive/polypropylene. Other metals, such as copper, steel, or brass, can also be used. Dissimilar metal examples are: aluminium/adhesive/copper, aluminium/adhesive/steel, and aluminium/adhesive/brass. Composite materials having metal/adhesive/polar polymer can also be made, for example, aluminium/adhesive/nylon or aluminium/adhesive/EVOH, or steel/adhesive/nylon/adhesive/steel. Other possible combinations will be readily apparent to those skilled in the art.

Such composite materials can be used to manufacture many different kinds of article. They can be used as packaging film, blow moulded bottles, coextruded sheet which can be thermoformed into containers, coatings on glass bottles or wood or metal or even to join two metals, either the same metal or dissimilar metals, into a lamination.

Blends of the graft copolymers with polypropylene and LLDPE may be formed by procedures similar to those described in U.S. Patents 4,087,587 and 4,087,588. It is preferred to prepare the grafted polyethylene first and then to blend it with the PP and LLDPE. The amount of graft copolymer in the blend is determined by the amount required to attain maximum adhesion to the substrate being used.

In order that the invention may be more fully understood, the following examples are given by way of illustration only. Of these examples, Examples 1—5 and 7 describe adhesive blends in accordance with the invention and for the purpose of comparison; Example 6 describes adhesive blends in accordance with the invention and blends not in accordance with the invention; Examples 8—10 describe adhesive blends in accordance with the invention; and Examples 11—14 describe composite structures in accordance with the invention.

In preparing the blends in these examples, any blending equipment or technique could be used. As an example, blends can be prepared in an electrically heated Brabender Plasticorder mixing head using a scroll-type mixer under the following conditions: temperature = 400°F., rotor speed = 120 rpm and mixing time = 10 minutes after flux.

All blends contained an antioxidant, for example 1,000 ppm tetrakis [methylene 3-(3',5'-di-tert butyl-4'-hydroxyphenyl)propionate] methane and 2,500 ppm distearyl thiodipropionate.

In specific examples, the resultant blends were compression-moulded into films approximately 0.005—0.007 inches thick. The films were then heat-sealed to the substrate under evaluation at an appropriate temperature and time. The conditions used were as follows:

1. Nylon 6 —430°F and 2 seconds
2. Ethylene-vinyl alcohol copolymer (EVOH) —430°F and 5 seconds
3. Polypropylene —500°F and 5 seconds
4. Aluminium —430°F and 2 seconds

The resulting composites were tested by cutting into strips one inch wide. Adhesion is then tested by a T-peel test similar to that described in ASTM D 1876—72.

All parts and percentages mentioned are by weight.

#### EXAMPLE 1

X-methyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride (XMNA) was reacted with a high density polyethylene homopolymer resin in a twin screw extruder to give a graft copolymer resin with 1.5% XMNA incorporation and a melt index of 1.6 g/10 min. The graft copolymer was blended in varying amounts with a random propylene-ethylene copolymer having a melt flow rate (MFR) of 2. T-peel adhesion results are summarized below:

	Graft Copolymer in Blend (%)	Adhesion to Nylon 6 (lbs/in)	
	3	0	
	5	0	
5	7	0	5
	10	0	

Adhesion of these blends to polypropylene is excellent (>10 lbs/in).

#### EXAMPLE 2

Using the same graft copolymer as described in Example 1, blends were prepared with a propylene-ethylene block copolymer having an MFR of 2. T-peel adhesion results are summarized below:

	Graft Copolymer in Blend (%)	Adhesion to Nylon 6 (lbs/in)	
	10	0.0	
15	15	0.3	15
	20	0.0	

#### EXAMPLE 3

The same blends as used in Example 2 were heat-sealed to an ethylene-vinyl alcohol copolymer (EVOH). All these blends gave extremely poor adhesion to EVOH. The samples could not be tested because they fell apart.

#### EXAMPLE 4

90% of a propylene-ethylene block copolymer containing 7.8% ethylene with an MFR of 3.4 was blended with 10% of the same graft copolymer as described in Example 1. This blend, when heat-sealed to EVOH and nylon 6, gave poor heat seal adhesion.

#### EXAMPLE 5

When a blend of 90% of a polypropylene homopolymer having an MFR of 4 with 10% of the same graft copolymer as described in Example 1 was heat-sealed to EVOH the resultant heat seal adhesion was 0.1 lb/in. If this same blend was heat-sealed to a random polypropylene copolymer as described in Example 1, its adhesion is greater than 10 lb/in.

The above examples show that if a polyethylene graft copolymer is blended with a polypropylene homopolymer, a random PP copolymer or a block PP copolymer the adhesion to polar polymers is not satisfactory.

#### EXAMPLE 6

A blend of a polypropylene block copolymer, a linear low density polyethylene and the graft copolymer described in Example 1, was prepared. The polypropylene block copolymer contained ethylene, had an MFR of 2 and a density of 0.902. The linear low density polyethylene contained butene-1, had an MI of 3 and a density of 0.922. The adhesion of blends containing various proportions of these materials was tested to nylon 6, EVOH and to a random polypropylene copolymer. The results are shown in Table I.

TABLE 1

PP	LLDPE	Graft Copolymer	Adhesion		
			Nylon 6 <sup>1</sup> lb/in	EVOH <sup>2</sup> lb/in	PP <sup>3</sup> lb/in
90	—	10	0.0	0.1	>10.0
65	25	10	2.1	1.2	>7.4
50	40	10	3.3	4.3	4.8
45	45	10	3.7	4.5	4.4
40	50	10	4.4	5.9	4.2
25	65	10	>8.7	8.6	0.5
—	90	10	>6.5	>8.1	0.8

1. 1 mil of nylon 6 was heat-sealed to 5—7 mil of the adhesive blend on a heat sealer at a set temperature of 430°F for 2 sec. The nylon 6 was closest to the heated jaw.

2. 5—7 mil of the adhesive blend was heat-sealed to 5—7 mil of EVOH at a heat sealer set temperature of 430°F. with the following order of layers starting with the upper heated jaw: 3 mil Mylar, adhesive blend, EVOH.

3. 5—7 mil of the adhesive blend was heat-sealed to 5—7 mil of PP at a set temperature of 500°F for 5 sec. with the following order of layers starting with the upper heated jaw: 10 mil Teflon, adhesive blend, PP, 10 mil Teflon.

It can be seen that there is a range of compositions containing less than 65% polypropylene and more than 25% polypropylene with which satisfactory adhesion to all three substrates could be obtained.

#### EXAMPLE 7

Blends containing the same graft copolymer as described in Example 1, the polypropylene block copolymer described in Example 6, and a polyethylene homopolymer made by the high pressure method, having a melt index of 1.8 and a density of 0.922, were prepared. T-peel adhesion to nylon 6, EVOH and the polypropylene random copolymer are shown in Table II.

TABLE II

PP	LDPE	Copolymer	Adhesion		
			Nylon 6 lb/in	EVOH lb/in	PP lb/in
90	—	10	0.0	0.1	>10
65	25	10	2.2	0.6	>10
45	45	10	1.8	1.4	5.6
25	65	10	—	3.5	0.4
—	90	10	4.1	—	0.0

Comparison of the T-peel adhesions obtained in Example 6 with those of Example 7 show that linear low density polyethylenes gave far superior adhesion results than those obtained with blends containing ordinary low density polyethylene.

## EXAMPLE 8

A blend was prepared containing 45% of a polypropylene block copolymer (MFR = 2, density = 0.992), 45% of a linear low density polyethylene (MI = 3, density = 0.922) and 10% of the graft copolymer described in Example 1. The blend (5—7 mil) was heat-sealed to 1 mil of "A wettability" aluminium at 430°F and 2 seconds. The T-peel adhesion was 3.4 lb/in.

## EXAMPLE 9

Maleic anhydride was reacted with a polyethylene resin in a twin screw extruder to give a graft copolymer resin incorporating maleic anhydride. 10% of this graft copolymer was blended with 45% of a propylene-ethylene block copolymer having an MFR of 2, and 45% of a linear low density polyethylene with a melt index of 3. This blend was adhered to various substrates with the following results in T-peel adhesion:

	Substrate	Adhesion lb/in	
	EVOH	6.3	
15	PP	3.5	15

## EXAMPLE 10

Bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride was reacted with a high density polyethylene homopolymer resin in a twin screw extruder to give a graft copolymer. 10% of this graft copolymer was blended with 45% of a propylene-ethylene copolymer having an MFR of 2 and 45% of an LLDPE with a melt index of 3. The T-peel adhesion results obtained are summarized below:

	Substrate	Adhesion lb/in	
	EVOH	7.2	
	PP	2.7	

## 25 EXAMPLE 11 25

A trilayer composite was prepared by heatsealing at 500°F for 5 sec. the following layers: nylon 6, a polypropylene adhesive of this invention (10% of the graft copolymer described in Example 1, 45% of a block polypropylene copolymer and 45% of a linear low density polyethylene), and a random copolymer of propylene and ethylene. The layers were arranged in the order given, i.e., nylon/adhesive/PP. The adhesion of the nylon to the adhesive layer was 2.7 lb/in with film tear and the adhesion of the adhesive layer to the polypropylene was 3.7 lb/in.

## EXAMPLE 12

A similar construction to that described in Example 11 was prepared using EVOH in place of polypropylene. The T-peel adhesion obtained to the nylon layer was 2.7 lb/in with tear of the nylon layer, and to EVOH was 7.5 lb/in with tear of the EVOH layer.

## EXAMPLE 13

A three-layer composite was prepared in a heat sealer at 500°F and 5 sec. using polypropylene/adhesive layer/EVOH as the three layers. The adhesive layer was described in Example 11. The T-peel adhesion results were:

	Substrate	Adhesion lb/in	
	PP	3.8	
	EVOH	5.1	

## EXAMPLE 14

A trilayer composite of PP/adhesive layer/aluminium was prepared in a heat sealer at 500°F and 5 sec. The adhesive layer was as described in Example 11. The following T-peel adhesion results were obtained:

Substrate	Adhesion lb/in
PP	4.0
EVOH	4.5

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## Glossary of Terms

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- EVOH — ethylene-vinyl alcohol copolymer  
 HDPE — high density polyethylene  
 LDPE — low density polyethylene  
 LLDPE — linear low density polyethylene  
 LPLDPE — low pressure low density polyethylene  
 MFR — melt flow rate, ASTM d 1238, condition L  
 MI — melt index, ASTM D 1238, condition E  
 PP — polypropylene  
 XMNA — x-methylbicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride
- 15 CLAIMS
1. A modified polyolefin adhesive blend, which comprises, by weight:
    - (a) 0.1 to 40 parts of a graft copolymer of 70 to 99.999% of a polyethylene backbone grafted with 30 to 0.001% of at least one polymerizable ethylenically unsaturated carboxylic acid or carboxylic acid anhydride, and
    - (b) 99.9 to 60 parts of a blending resin mixture of 25 to 75% of a linear low density polyethylene and 75 to 25% of a polypropylene.
  2. An adhesive blend according to claim 1, in which the linear low density polyethylene is a copolymer of ethylene and up to 40% of propylene, butene-1, hexene 1 or octene-1.
  3. An adhesive blend according to claim 1 or 2, in which the linear low density polyethylene has a narrow molecular weight distribution.
  4. An adhesive blend according to any of claims 1 to 3, in which the polypropylene is a copolymer of propylene and ethylene.
  5. An adhesive blend according to any of claims 1 to 4, in which the grafting monomer used to form the graft copolymer is at least one of acrylic acid, methacrylic acid, maleic acid, itaconic acid, citraconic acid, mesaconic acid, maleic anhydride, 4-methyl cyclohex-4-ene-1,2-dicarboxylic acid anhydride, bicyclo(2.2.2)oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,3-dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro(4.4)non-7-ene, bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride, maleopimaric acid, tetrahydrophthalic anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride, Nadic anhydride, methyl Nadic anhydride, Himic anhydride, methyl Himic anhydride, and x-methyl bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride.
  6. A composite structure comprising a substrate and, adhered thereto, a layer of a modified polyolefin adhesive blend according to any of claims 1 to 5.
  7. A composite structure according to claim 6, in which the substrate is formed of a polar polymer, metal, glass, paper, wood or cellophane.
  8. A composite structure according to claim 6 or 7, in which the substrate is formed of nylon, ethylene-vinyl alcohol polymer or aluminium.
  9. A composite structure according to any of claims 6 to 8, in which a second substrate layer is adhered to the surface of the adhesive blend layer remote from said first substrate.
  10. A composite structure according to claim 9, in which the second substrate is formed of a propylene homopolymer or copolymer.
  11. A modified polyolefin adhesive blend according to claim 1, substantially as herein described in any of Examples 6 and 8 to 10.
  12. A composite structure substantially as herein described in any of Examples 11 to 14.